

1991 Annual Report

RESEARCH AND DEVELOPMENT

**Laboratory Services Branch
Ontario Ministry of the Environment**

September, 1992

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Overview

Ray E. Clement, Chair, R&D Committee

To support the work of the Ministry of the Environment, the Laboratory Services Branch reports the analytical results from some 2,000,000 tests each year. The types of samples analyzed include fish, surface and drinking water, soil, landfill leachates, ambient air, hazardous waste, and many others. The work performed by the Laboratory Services Branch is highly complex and ever-changing. New sample types are often encountered, and each year new analytes are added to our monitoring list. Our work generates the data that are essential for our clients to study the Ontario environment and to make informed regulatory decisions.

Whether we are asked to determine a new analyte, analyze a unique type of sample, or improve the detection limits or quantitative accuracy of our existing methods, our principal goal is to improve the service to our clients. To deliver the high quality analytical services they need requires an ongoing program of applied research and development (R&D). The environmental analysis field is growing and changing so rapidly that the only way to keep up with developments in some areas is to be one of the leaders through R&D studies. Therefore, our applied R&D efforts are also an important means of ensuring that key areas of our operation are state-of-the-art.

In this report are described the principal applied R&D studies that were conducted in 1991. In addition to these investigations, many small methodology improvements are introduced by our staff on a regular basis in the normal course of their work. All of these improvements are necessary to ensure the Ministry of the Environment receives the high quality analytical data so necessary to its various operations. The report is organized according to the various areas supported, rather than by areas of technology, to enable our clients to better see how they are being served.

Air Resources Branch Support

Introduction

Our current R&D support for the Air Resources Branch is in the area of airborne toxics. The measurement of such compounds as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), and the chlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) in ambient air and atmospheric deposition is needed to understand their transport and fate in the environment. The analysis of such compounds is difficult because they are often present at very low concentrations.

I. PCDDs and PCDFs in Ambient Air

Study Leader: R.E. Clement

Study Team: C. Tashiro, T. Gobran, L. Grey, H. Bonek-Ociesa, E. Reiner

Introduction and Objectives

This project is a collaborative effort between the Laboratory Services and Air Resources Branches of the Ministry of the Environment, and Environment Canada. It is supported by the Canadian Council of Environment Ministers (CCEM). The overall coordinator for CCEM is Mr. Tom Dann of Environment Canada. The objectives of this work were to:

- ☐ develop reference methods for PCDDs/PCDFs in ambient air
- ☐ survey ambient air PCDD/PCDF methods reported by others and develop a database of centres of excellence and of reported PCDD/PCDF data

- ☐ transfer the technology to other Canadian government agencies and the private sector
- ☐ perform round-robin studies to determine the state-of-the-art for the determination of PCDDs/PCDFs in ambient air

Results

Methods for PCDDs and PCDFs in ambient air were developed and are currently on-line at both the Environment Canada River Road laboratory and the Ministry of the Environment, Laboratory Services Branch Dioxin Laboratory. A data base of Centres of Excellence for this application and of the PCDD/PCDF ambient air data reported in the literature was prepared by Wellington Environmental Laboratories under contract to the Ministry of Environment. A report is in preparation to describe the sampling and analysis methods used for PCDDs/PCDFs in ambient air - based on a workshop held in conjunction with the Dioxin'89 international conference hosted by the Ministry of the Environment. An 18-laboratory round-robin study was conducted to determine the analytical state-of-the-art for testing PCDDs/PCDFs in ambient air. Modifications to the GC-MS method were introduced to permit the isomer-specific determination of all 17 2,3,7,8-substituted PCDDs/PCDFs, in addition to the group totals.

Work to be Completed

The PCDD/PCDF workshop report is nearing completion. It will be a reference document that describes all aspects of the analysis including sampler siting, sampling, sample preparation, gas chromatography-mass spectrometry analysis, and quality assurance/quality control (QA/QC). Data analysis of the ambient air round-robin results is underway and will be completed early in 1992. Modifications to the GC-MS analysis method for the isomer-specific determination of the 17 toxic PCDDs/PCDFs, in addition to the group totals, must be completed. An investigation of the stability of PCDDs/PCDFs during storage on the sampling materials is needed.

Publications and Presentations

1. C. Tashiro, R. Clement, A. Szokolcai and W. Chan. *Evaluation of Monitoring Techniques for Dioxins in Ambient Air*; Proceedings of the Annual Technology Transfer Conference

- (ISSN 0825-4591), Part D - Analytical Methods; Environment Ontario, Toronto, Canada, Nov. 1987.
2. C. Tashiro, R. Clement and W. Chan. *Evaluation of High-Volume Sampling Techniques for the Determination of CDD/CDF in Ambient Air*; Proceedings of the 1988 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants; Research Triangle Park, North Carolina, May 1988; pp. 621-628.
 3. T. Dann, C. Chiu, R. Lao, C. Tashiro, R. Clement, A. Szokolcai and W. Chan. *Intercomparison Study of Ambient Air Dioxin/Furan Sampling and Analytical Methods*; Proceedings of the 1988 EPA/APCA International Symposium on Measurement of Toxic and Related Air Pollutants; Research Triangle Park, North Carolina, May 1988; pp. 621-628.
 4. C. Tashiro, R. Clement, A. Szokolcai and W. Chan. *Comparison of High Volume Sampling Techniques for Dioxins and Furans in Ambient Air*; Chemosphere, 1989, 19, 1-6.
 5. P. Steer, R. Clement, C. Tashiro, M. Lusi, T. Dann, C. Chiu and M. Bumbaco. *Development of Ambient Air Monitoring Methodologies for Dioxins and Furans*; Proceedings of Technology Transfer Conference (ISSN 0825-4591), Volume 1; Environment Ontario, Toronto, Canada 1989; pp. 67-74.
 6. P. Steer, C. Tashiro, R.E. Clement and M. Lusi. *Ambient Air Sampling of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Ontario: Preliminary Results*; Chemosphere, 1990, 20, 1431-1438.
 7. C. Tashiro, R.E. Clement, S. Davies, T. Dann, P. Steer, M. Bumbaco, B. Oliver, T. Munshaw, J. Fenwick, B. Chittim and M.G. Foster. *Ambient Air Analysis Round-Robin*; Chemosphere, 1990, 20, 1319-1324.
 8. D. Waddell, B. Chittim, R. Clement, C. Tashiro, S. Davies, A. Szokolcai, P. Steer and T. Dann. *Database of PCDD/PCDF Levels in Ambient Air and in Samples Related to the Pulp and Paper Industry*; Chemosphere, 1990, 20, 1463-1466.

II. Determination of Trace Organics in Atmospheric Deposition

Study leaders: B. Foster and R. Clement

Study Team: L. Grey, O. Ting, H. Bonek-Ociesa, T. Kolic, E. Reiner, P. Yang

Introduction and Objectives

It is now known that toxic organics - even those considered relatively non-volatile - are spread in the environment by long-range atmospheric transport and deposition. It is important to study the concentrations of these chemicals that are deposited in Ontario through rainfall and snowfall, so we can evaluate the sources of and human exposure to these chemicals. The objectives of this work were to:

- ☐ develop the methodology needed to analyze precipitation samples for trace levels of toxic organics including PCDDs, PCDFs, PAH, PCBs
- ☐ develop a database of these chemicals in precipitation samples from Ontario urban and rural locations

Results

The analytical methodology has been evolving over the past 3 years. Sampling stations have been established at Dorset, Toronto Island, and Windsor, and samples are collected monthly. Analysis of precipitation samples is difficult because the sample size is variable, it is difficult to ensure that no extraneous material is collected along with the precipitation, and low detection limits must be achieved.

Studies on the use of filters followed by sorbent cartridges to collect samples instead of 20-gallon jugs were carried out. Results showed that the trapping and extraction of analytes from the filters and sorbent cartridges is at least as efficient as collecting precipitation in large jugs to be transported to the laboratory for liquid-liquid extraction. Since handling, transport, and extraction of the sorbent cartridges is much simpler and quicker, this method of sampling was adopted. Additional preliminary investigations showed that PCDDs and PCDFs in solvent rinsings from the funnel used for sampling are significant - in some cases greater than the quantities of PCDD/PCDF found in the precipitation sample itself. Laboratory studies were initiated to test if PCDDs and PCDFs were adsorbed onto the funnel walls during sampling, and

whether the choice of solvents affected the efficiency of recovering the PCDDs/PCDFs by repeated funnel rinsings. Based on this work acetone was chosen as the solvent to be used for funnel rinsing in the field, and the use of methylene chloride was discontinued.

Work to be Completed

Further studies on the adsorption of PCDDs/PCDFs on the sampler funnel walls are needed to better quantify the fraction of analytes adsorbed, and whether solvent rinsing with acetone is sufficient for quantitative recovery of the adsorbed analytes. Continued monitoring at the sampling sites is needed to expand the data base for Air Resources Branch modelling studies.

Publications and Presentations

1. C. Tashiro, R. Clement, M. Lusi, D. Orr and N. Reid. *Dioxins and Furans in Toxic Precipitation Samples*; Proceedings of the Annual Technology Transfer Conference (ISSN 0825-4591), Part D - Analytical Methods; Environment Ontario, Toronto, Canada, Nov. 1987.
2. C. Tashiro, R.E. Clement, M. Lusi, D. Orr, and N. Reid. *Monitoring Dioxins and Furans in Precipitation Samples*; presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, Nevada, October 4-9, 1987.
3. C. Tashiro, R.E. Clement, N. Reid, D. Orr, and M. Shakleton. *Determination of Dioxins and Furans in Precipitation Collected in Urban and Rural Ontario Locations*; presented at the 8th International Conference on Chlorinated Dioxins and Related Compounds, Umea, Sweden, August 21-26, 1988.
4. C. Tashiro, R.E. Clement, M. Lusi, D. Orr and N. Reid. *Monitoring Dioxins and Furans in Precipitation Samples*; Chemosphere 1989, 18, 777-782.
5. C. Tashiro, R. Clement, N. Reid, D. Orr and M. Shakleton. Chemosphere, 1989, 19, 535-540.

6. N.W. Reid, D.B. Orr, M.N. Shackleton, M.A. Lusi, C. Tashiro and R. Clement. *Monitoring Dioxins and Dibenzofurans in Precipitation in Ontario*; Chemosphere, 1990, 20, 1467-1472.
7. C.H.M. Tashiro, P.J. Steer, M.L. Shackleton, R.E. Clement, and N.W. Reid. *Dioxins and Furans in Wet and Dry Deposition in Ontario*; peer-reviewed proceedings of the 84th Meeting of the Air & Waste Management Association, Vancouver, B.C., June 1991.

Water Resources Branch Support

Introduction

The protection of drinking water quality has been and will continue to be one of the most important issues facing the Ministry of the Environment, and therefore the Water Resources Branch has many programs that are supported by analytical measurements. New contaminants are occasionally added to monitoring lists, and there is an ongoing push towards lower detection limits and increased sample throughput. Several R&D studies have been initiated to deal with these issues.

I. Improved Extraction Methods

Study Leaders: W. Offenbacher, K. Taylor
Study Team: O.W. Berg, P. Crozier

Introduction and Objectives

Developing improved extraction methods for trace organic pollutants is an ongoing activity. This work is needed in part because the low detection limits that are required for some chemicals can only be obtained by extraction of several liters of sample; but in addition, methods that are more rapid and rugged contribute to improved sample throughput and quality control. Some newer sample preconcentration methods can also help the "greening" of the laboratory by reducing our dependence on large volumes of solvents - which also may lead to reduced operating costs.

Two separate extraction studies are underway. The first, under the direction of M. Lawrence, is examining the possibility that organochlorine pesticides can be extracted efficiently from water by using only one milliliter of solvent instead of 180 mL. In a second investigation, K. Taylor is examining the use of special filtering media (empore disks) to see whether efficient and rapid extraction of dioxins from large volume water samples (4-10 L) can be performed.

Results

Basic experimental work has shown that the efficient extraction of 1.0-liter water samples by using only 1mL of solvent is possible for hydrophobic contaminants such as organochlorine pesticides. Experimentally, the extractions are performed by mixing solvent and samples on a roller apparatus. This is a more rugged and reproducible procedure than stirring or shaking and can be done unattended. The laboratory portion of breakthrough studies on dioxins/furans from empore disks have been completed.

Work to be Completed

Validation and other quality control studies must be completed to show that the current 180 mL solvent extraction method for organochlorine pesticides can be replaced by 1.0 mL of solvent. Kinetic studies on the roller extraction and validation of the total method need to be done. Data interpretation for the GC-MS analysis of samples from empore disk breakthrough studies must be finished. Further experimental work plans will be based on the results of these initial studies.

II. Metals in Surface Waters by ICP-MS

Study Leader: M. Powell
Study Team: E. Quan, L. Liu

Introduction and Objectives

Surface waters present a challenge for ICP-MS analysis because of the presence of dissolved particulates. The objective of this study is to develop a routine ICP-MS method for this application. If successful, the new ICP-MS method would replace the current preconcentration method. This would result in much better accuracy, faster turnaround, improved quality control, and would be about 50% of the cost of the current method.

Results

A new method was developed that compensated for matrix effects due to the presence of dissolved particulates by using internal standards. Detection limits have been improved from 10 to 50 times over those obtained by using ICP/OES without the need for sample preconcentration.

Work to be Completed

The experimental work on the method development part of this study is complete. Currently, a comparison study of the new method and existing method is underway. A final report and new method documentation are in preparation.

III. Method Development for MISA Group 29

Study Leader: P. Wee
Study Team: S. Matthew

Introduction and Objectives

To support monitoring requirements of the MISA program, a method for elements in nitric acid digestable samples is needed. This method, when completed, will be capable of performing the open characterization analysis of complex liquid samples.

Results

Sludge samples were oven-dried at 110°C and acid-digested by using nitric acid. Where elements were present in the organic form, it was necessary to add H₂O₂ to the digestate to achieve reproducible dissolution. Ashing samples was investigated but was not found to be necessary. The digestion and analytical procedure was sufficient for the determination of about 48 elements. Instrument calibration procedures and method detection limits have been determined for all 48 elements. Method documentation for this application is in preparation.

Work to be Completed

Attempts will be made to extend the applicability of the method to additional elements. The procedure will be tested for applicability to the analysis of municipal sludges, and some additional method modifications may be required.

IV. Enumeration of Bacteria

Study Leader: M. Young
Study Team: G. Horsnell

Introduction and Objectives

The enumeration of environmental bacteria from aqueous samples is generally performed by manual counting of bacterial colonies after filtration. In this project, an image analyzer for the enumeration of bacterial colonies on membrane filters will be developed. The final output of the work is expected to be an automated system that will increase sample throughput and achieve better precision.

Results

So far, results indicate that the image analyzer cannot readily distinguish individual bacterial colonies that occur in clusters. The machine therefore produces counts significantly different than those obtained by manual counting.

Work to be Completed

A new software program is being developed by the instrument manufacturer that should resolve the cluster problem. Once the new program is installed the automated enumeration will again be compared to manual counting. Once proven for fecal coliform colony counting, attempts will be made to apply the new method to other bacterial parameters.

V. PAH Storage Study

Study Leader: P. Crozier
Study Team: J. Yang, L. Gurprasad, L. Matchuk

Introduction and Objectives

It was observed that polycyclic aromatic hydrocarbons (PAH) spiked into heavily chlorinated water samples could not be detected after samples were stored for several days. This study was initiated to determine how samples could be stored to eliminate this effect.

J. Yang is a visiting scientist from Shaanxi Environmental Monitoring Central Station, Xi'An, China.

Results

Experimental work has been completed. Addition of sodium thiosulphate to samples of chlorinated waters was found to extend their storage time to at least two months with no observable PAH degradation. A draft report has been prepared.

Work to be Completed

The report will be completed, and the new procedure incorporated into the standard method documentation. Results of this work will be presented at the Ministry's annual *Technology Transfer Conference*.

VII. New Method for NDMA Determination

Study Leader: P. Crozier
Study Team: E. Williams

Introduction and Objectives

Dimethyl nitrosamine (NDMA) is a potential groundwater contaminant that recently has been detected in some Ontario locations. An effective method was developed that uses high resolution mass spectrometry (HRMS) as the final detection step. This sophisticated and expensive instrumentation was mandatory because of the low parts-per-trillion detection limits required for NDMA in water. To increase sample throughput, lower the cost of NDMA testing, and provide greater analytical capability, this project was initiated. By using selective derivatization and gas capillary chromatography with sensitive detection, it is hoped that a non-HRMS method can be developed that can meet the performance characteristics of the existing method.

Results

The development of a salicylaldehyde/NDMA derivatization method amenable to routine analysis by low resolution quadrupole mass spectrometry (LRMS) was investigated. The derivatization method involves reduction of NDMA to the unsymmetrical hydrazine, its distillation from the sample matrix and its subsequent reaction with salicylaldehyde to form the stable salicylaldehyde dimethylhydrazone (SDMH) derivative. The derivatization of NDMA to the corresponding higher molecular weight hydrazone and its subsequent analysis gives the potential method an extra measure of specificity as well as reducing low molecular weight LRMS interferences.

The SDMH derivatization method, when deuterated NDMA is used as an internal standard, provided reasonable analytical results. Although the recovery and precision of individual analytical steps was more than acceptable, the large number of manipulation steps involved and the additive nature of recovery/precision errors made whole method precision less than anticipated. Average results of 14.9 ng \pm 3.3 ng were obtained for forty-seven 10ng

NDMA spikes processed over a six month period. Elevated NDMA background levels were noted with the SDMH derivatization method. After background subtraction, results generated by the SDMH derivatization method for effluent samples were similar to those obtained by using the standard liquid/liquid extraction method.

The SDMH derivatization method does have some limitations for application to routine drinking water samples. Only six samples can be processed per day (per technician), and the method precision is only barely adequate, especially at the low concentrations needed to monitor NDMA in drinking water. A better approach may be to use a liquid/liquid internal standard extraction method, followed by multidimensional gas chromatography-mass spectrometry.

Work to be Completed

The project is complete. A draft report is being circulated for technical review.

VIII. Analysis of Sewage Sludges for Organic, Extractable Priority Pollutants

Study Leader: R. Lega
Study Team: J. Ladwig, O. Meresz

Introduction and Objectives

Sewage sludge is one of the most difficult sample types to analyze for trace levels of organic pollutants. As more attention is focused on municipal waste treatment, the importance of developing sound analytical methods for organics in sewage sludge is growing. In this project, a method for some 98 target organic compounds in sewage sludge is to be developed. These target compounds include polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCs), chloroaromatics, phenols, and phenoxy acids (PA). The required studies include the development and optimization of an effective extraction scheme, removal of interferences from sample extracts, and gas chromatographic separation of individual analytes - including an evaluation of derivatization techniques for phenolic and phenoxy acid compounds.

Results

The extraction of organics from sludge was assessed through real-matrix spiking studies. Several extraction procedures were investigated, including in-situ derivatization and extraction followed by derivatization. Optimization studies included the evaluation of suitable solvents/solvent mixtures, methods of homogenization, pH, and phase separation by using such techniques as centrifugation, salting out and use of a separatory funnel.

After homogenization of the sludge sample by physical mixing, extraction is performed by using a variety of solvents, followed by centrifugation. Interfering co-extractives are removed by column chromatography using gel permeation and Florisil, followed by sulphur removal. After derivatization of acidic analytes including phenols, target compounds are determined by using GC/MS. Recoveries for most compounds in spiking studies ranged from 50% - 90%.

Work to be Completed

Although most target organics can be determined by using this procedure, some improvements are needed to improve the results for a few analytes such as cresols and some phenols. In addition, the recoveries of aldrin and indole were inconsistent. Quality control data must be generated for the phthalates.

Multi-Program Support

Introduction

Many analytical methods support a number of programs and Branches. For example, R&D work to improve the precision of gas chromatography-mass spectrometry determinations will benefit all LSB clients who submit samples for the determination of organic pollutants. Sometimes these projects are started because of a specific client request (i.e. to reach lower detection levels), but often such studies are initiated by LSB staff as an ongoing effort to improve analytical capability and to bring on-line new technologies that will benefit our clients by providing faster turnaround, increased sample capacity, better specificity, or improved accuracy and precision.

I. Mercury Determination by ICP-MS

Study Leader: M. Powell

Study Team: E. Quan, D. Wiederin, D. Boomer

Introduction and Objectives

Direct Injection Nebulization (DIN) is a new sample introduction system for Inductively Coupled Plasma (ICP) that increases efficiency of sample transport to the plasma. The Ministry of the Environment, Laboratory Services Branch, has been a beta-test site for this new technology. Use of this technology will result in a more efficient use of complex, expensive ICP-MS instrumentation and faster sample turnaround for our clients. The new methodology

could save 1.5 staff-years in sample preparation time and result in improved quality control, faster sample turnaround, and lower cost.

Results

A crude "home-built" apparatus was constructed to test the feasibility of mercury determination by DIN. By use of the DIN, sample transport efficiency to the plasma is increased. A noticeable reduction in memory effects in the determination of mercury was observed. Therefore, a reduction of time and labour was effected over the conventional technique. These initial studies showed that a good potential exists for this technique. Further investigations are on-going.

Work to be Completed

Continued investigations of the DIN technique are underway. Emphasis will be placed on the evaluation of commercially available equipment.

Publications and Presentations

1. M. Powell, E. Kuan, D. Boomer, and D. Wiederin. *An Environmental Application Using ICP-MS and Direct Injection Nebulization for the Hg Analysis of Drinking Water: Analytical Chemistry, submitted for publication.*

II. Ion Chromatography ICP-MS

Study Leader: M. Powell

Study Team: J. Hipfner

Introduction and Objectives

Currently, the capability to determine heavy metals (Cd, Hg, Pb, Cu) at background concentrations does not exist - because existing methods cannot reach the low detection limits required. Because some of these metals may be toxic at background concentrations, it is important to lower our detection limits for samples such as precipitation and surface waters. By using the leading-edge technology of Ion Chromatography ICP-MS, it may be possible to lower our current detection limits by a factor of 10. This method development is needed to support the APIOS program.

Results

A feasibility study has been completed. A technique was developed to preconcentrate Cd, Cu, and Pb from a water matrix. The detection limit improvement for ICP-MS was 50-100 X that of the existing method. In addition an automated, computer-controlled sampling system was developed.

Work to be Completed

This project demonstrated that the desired detection limit improvements are possible by application of the chosen technology. Full implementation of a routine, automated system requires acquisition of additional commercially-available instrumentation.

Publications and Presentations

1. D. Boomer, M. Powell, and J. Hipfner. *Characterization and Optimization of HPIC for On-line Preconcentration of Trace Metals and Detection by ICP-MS*; Talanta, 1990, 37, 127-134.

III. Multidimensional Chromatography

Study Leader: P. Crozier

Introduction and Objectives

This technology has the potential to greatly improve specificity and to lower detection limits - without the need for mass spectrometric detection. It also may be possible to increase the number of compounds analyzed per sample, which could significantly improve sample throughput. The basis of the technology is simple; instead of passing the sample through a single gas chromatography column where analytes are separated and detected, two or more columns are chosen for the separation so that much more efficient separations are possible. Environmental samples are so complex that it is seldom possible to completely separate all analytes from each other, therefore any technology that can improve analyte separation will achieve improved precision and accuracy. In addition, lower detection limits can be achieved by injecting large sample extract volumes on the initial column and then cryofocussing only the small portion of compounds of interest on the head of the second column - that will be used for the analytical separation.

Results

Scientific Glass Engineering Inc. (SGE) multidimensional chromatography hardware was installed on a Hewlett Packard 5890 GC/5971A MSD system. The SGE/HP MSD system was evaluated for its application to routine pesticide analysis as a viable alternative or complementary technique to electron capture, nitrogen/phosphorus, or flame ionization GC detectors.

Good quantitation and retention time reproducibility were obtained with the SGE/HP MSD system with multiple 5uL manual injections and manual SGE program initiation. Relative standard deviations of 0.14% and 4.7% were obtained for retention time and peak area quantitation, respectively. It is expected more consistent retention times and quantitation could be produced if the SGE and HP systems were completely integrated and automated (i.e. autosampler injection with automated SGE program initiation).

Work to be Completed

Since HP7673 autosampler syringes in excess of 25uL are not available, low-level instrument sensitivity requires multiple injections with oven/cryotrap programming being done between autosampler injections. The next logical step in analytical system development is testing with larger injection volumes (<10uL) multiple manual injections. Work is now proceeding to fully automate the two systems and test the integrated system with multiple large volume injections for possible inclusion in routine pesticide analytical schemes.

Publications and Presentations

1. Patrick W. Crozier. *Development and testing of a Multidimensional Chromatographic/Mass Spectrometric Detection System for Trace Level Pesticide Analysis*; Ontario Ministry of the Environment, Laboratory Services Branch Internal Report, Rexdale, Ontario, 1991.

IV. LC-MS Analysis of Environmental Samples

Study Leader: V. Taguchi

Study Team: C. Koester

Introduction and Objectives

For the determination of organic pollutants in environmental samples, gas chromatography-mass spectrometry (GC-MS) is generally used. However, GC-MS is only applicable to about 15% of known organic compounds. High molecular weight compounds, easily decomposed compounds, and highly polar compounds are difficult to determine by using GC-MS. Liquid Chromatography-Mass Spectrometry (LC-MS) is capable of determining many of these substances. LC-MS is an emerging technology, and considerable effort will be required to optimize the system and to analyze real samples. The goals of this project are to optimize an HP 1090 LC - VG Trio2 MS system with particle-beam interface for the identification of target compounds and unknown compounds in environmental samples.

Results

Under the Postdoctoral Fellowship program of the Ministry of Environment, Ms. C. Koester joined LSB in December to work on optimizing the LC-MS system. Routine operating conditions for the LC-MS system were established and a list of critical parameters for both LC and MS to ensure reproducible system operation were determined. In a real environmental sample of sewage treatment plant effluent, N,N'-diphenyl urea, N,N'-ethanedione and elemental sulphur were detected by LC-MS, but were *not* detected in routine GC-MS analysis. A major limitation in the characterization and quantitation of components in environmental samples is that analyte response depends on the LC mobile phase composition.

Work to be Completed

Detailed detection limit studies will be conducted for a variety of pesticides. The use of buffers to increase analyte transport efficiency across the LC-MS interface will be examined. The use of LC-MS for identifying organics not amenable to GC-MS determination will continue, and the application of LC-MS for quantitative determination of organics for which no GC-MS methods exist (i.e. glyphosate) will be examined.

Publications and Presentations - 1991

Laboratory Services Branch

1. R.E. Clement, K. Michael Siu and H.H. Hill, Jr., Editors, "Instrumentation For Trace Organic Monitoring", Peer-Reviewed Proceedings of a Symposium From the 3rd Joint Chemical Congress, June 1988, Lewis Publishers, 1991.
2. R.E. Clement, M. Langhorst, and G.A. Eiceman. "Environmental Analysis"; Anal. Chem., 1991, 63, 270R-292R.
3. C.H.M. Tashiro, P.J. Steer, M.L. Shackleton, R.E. Clement, and N.W. Reid. Dioxins and Furans in Wet and Dry Deposition in Ontario, peer-reviewed proceedings of the 84th Meeting of the Air & Waste Management Association, Vancouver, B.C., June 1991.
4. R.E. Clement. "Dioxin Analysis State-of-the-Art: The Study of Multimedia Contaminants"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume 1; Environment Ontario, Toronto, Canada 1991; pp. 7-13.
5. R.E. Clement. Dioxin Analysis: 30 Years of Advances, Anal. Chem. 1991, 63, 1130A-1139A.
6. R.E. Clement, "Ultra-Trace Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (Dioxins) Analysis: Thirty Years of Advances", invited talk presented at the 1991 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, March 4, 1991.
7. R.E. Clement, "Solving Difficult Analytical Problems: Dioxin in Water", invited talk to be presented at the 74th Canadian Chemical Conference, Hamilton, June 3, 1991.

8. *R.E. Clement*, "Ultra-Trace Determination of the Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Water Samples", invited plenary talk presented at the Canadian Spectroscopy Society Conference, Ottawa, August 12, 1991.
9. *R.E. Clement* and *C. Tashiro*, "Forest Fires as a Source of PCDD and PCDF", invited talk presented at the 11th International Symposium on Chlorinated Dioxins and Related Compounds, Research Triangle Park, North Carolina, September 23-27, 1991.
10. *S. Ramamoorthy* and *R.E. Clement*, "Scoring System to Evaluate Interlaboratory Performance for the Analysis of Dioxins and Furans in Fish Tissues", poster presented at the 11th International Symposium on Chlorinated Dioxins and Related Compounds, Research Triangle Park, North Carolina, September 23-27, 1991.
11. *G.M. Charbonneau*, *T.L. Collier*, *W.G. Craig*, *C.J. Morin*, and *C.D. Hall*. "Development of an Enzyme Immunoassay for the Rapid Detection and Quantification of Glyphosate"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 694-697.
12. *T.S. Thompson*, *T.M. Kolic*, and *K.A. MacPherson*. "Dual-Column High Performance Liquid Chromatographic Cleanup Procedure for the Determination of Polychlorinated Dibenzo-p-dioxins in Fish Tissue"; *J. Chromatogr.* 1991, 543, 49-58.
13. *Eric J. Reiner*, *David H. Schellenberg*, and *Vince Y. Taguchi*. "Environmental Applications for the Analysis of Chlorinated Dibenzo-p-dioxins and Dibenzofurans Using Mass Spectrometry/Mass Spectrometry; *Environ. Sci. Technol.* 1991, 25, 110-17.
14. *R.R. Martin*, *J. Li*, *T. Lee*, *M. Guiliacci*, *P. Wong*, *J. Hipfner*, and *R. Moody*. "Analysis of Spatial and Temporal Distribution of Inhaleable Air Particulates in Ontario"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 75-84.
15. *Z. Mino*, *M. Yang*, *J. Pawliszyn*, and *I. Ahmad*. "Supercritical Fluid Extraction with Simultaneous Class Fractionation of PCBs and PAHs from Adsorbent Materials for Air Pollution Determinations"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 672-675.

16. K.T. Taylor, R.S. Mercer, H. Bonek-Ociesa, and E.J. Reiner. "Automation of a Dual Open Column Chromatographic Cleanup Technique for Samples Containing Chlorinated Dibenzo-p-Dioxins and Dibenzofurans"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 711-714.
17. T.M. Kolic, K.A. MacPherson, E.J. Reiner, and T.S. Thompson. "An Automated High Performance Liquid Chromatographic Cleanup Procedure for the Determination of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 715-719.
18. V.Y. Taguchi, E.J. Reiner, D.T. Wang, J.-P. Palmentier, and S.W.D. Jenkins. "A Study of Chemical Interferences in the Analysis of N-Nitrosodimethylamine in Environmental Samples"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 720-723.
19. J. Semmler, P. Yang, and G. Crawford. "A Turn-Key FTIR System for the Analysis of Gas Phase Polychlorinated Biphenyls"; Proceedings of the Technology Transfer Conference (ISSN 0825-4591), Volume I; Environment Ontario, Toronto, Canada 1991; pp. 724-729.
20. I. Ahmad, J. Bodnar, and G. Ladwig. "Organic Contaminants Analysis - Application of High Performance Liquid Chromatographic Cleanup of Environmental Samples", presented at the Spectroscopy Society of Canada, Southern Ontario Section meeting, Toronto, Ontario, May 16, 1991.
21. B. Foster, B. Kanabe, O. Ting, P. Yang, M. Shackleton, and N. Reid. "A Study of Polynuclear Aromatic Hydrocarbons in the Great Lakes Deposition Basin", presented at the 84th Air and Waste Management Association meeting, June 16-21, 1991.
22. J. Semmler, P.W. Yang, and G. Crawford. "Gas Chromatography/Fourier Transform Infrared Studies of Gas-Phase Polynuclear Aromatic Hydrocarbons"; Vibrational Spectroscopy 1991, 189-203.

23. M.J. Yang and P.W. Yang. "An IBM-PC Based Computer Program for the Analysis of Infrared Spectra"; *Applied Spectroscopy* 1991, 45, 1739-44.
24. C.H. Marvin, I.D. Brindle, C.D. Hall, and M. Chiba. *J. Chromatogr.* 1991, 555, 147-54.
25. V.Y. Taguchi, E.J. Reiner, D.T. Wang, J.-P. Palmentier, and S.W.D. Jenkins. "A Comparison of Low Resolution and High Resolution Mass Spectrometric Techniques for the Determination of N-nitrosodimethylamine in Environmental Samples"; Presented at the 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tennessee, May 1991.
26. D. Robinson, K.-P. Ngo, J.-P. Palmentier, E.J. Reiner, and V.Y. Taguchi. "An Investigation of Ionization Techniques Applied to the Analysis of 2-Methylisoborneol (2-MIB) and Geosmin"; Presented at the 38th Canadian Spectroscopy Conference, Ottawa, Ontario, August 1991.
27. G.E. Horsnell, M. Young, and J.E. Pagel. "Characterization of Aerobic Heterotrophic Bacteria Isolated from Marshes"; *Environmental Toxicology and Water Quality*, 1991, 6, 329-40.
28. J.A. Clark. "Comparison of the New Simplified Bacteriological Testing and Conventional Bacteriological Analysis"; Presented at the American Water Works Association, Southern Ontario Section, Joint Annual Conference, Hamilton, Ontario, April 28 - May 1, 1991.
29. M.W. Rawlings. "Regression Techniques for Analytical Chemistry Technicians"; Environment Ontario, Laboratory Services Branch, Water Quality Section Internal Report, January, 1991.



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